

Vanadyl VO(II) with o-phenylenediamine complexes: preparation and spectral characterization

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Abstract

Two dinuclear vanadyl VO(II) complexes with o-phenylenediamine (OPD) ligand have been prepared. The complexes have been characterized by different techniques such as FT-IR, UV-Vis and mass spectroscopy, magnetic susceptibility and molar conductivity. The obtained FTIR data show that the o-phenylenediamine ligand coordinated from two nitrogen atoms of amine groups. The mass spectral data show that the vanadyl VO(II) complexes are dinuclear and the o-phenylenediamine ligand binds the two vanadium atoms as a bridge ligand.

The magnetic susceptibility measurements indicate that the complexes are paramagnetic. UV-Vis measurements show the peaks of the charge transfer and the metal (d-d) transitions. From all spectroscopic data, square pyramidal structures have been proposed for the complexes.

Keywords: Vanadyl VO(II) complexes, o-phenylenediamine, dinuclear complexes, magnetic susceptibility, FTIR spectroscopy.

Introduction

Vanadium metal is a group 3d transition metal and has definite chemical and biochemical properties¹. Vanadium occurs in different oxidation states with the ability to participate in reactions involving the formation of free radicals. The most essential oxidation states of the vanadium are V(III), V(IV) and V(V). The two most biologically and physiologically stable states are vanadyl VO(II) and vanadate V(V)^{2,3}. Vanadium is possessing a well-defined geometry of its inner coordination sphere, regarding the usual oxidation states of the metal V(IV) and V(V)⁴. Vanadium complexes with a rapid exchange of donor atoms in a coordination scope are characterized as 'labile'; in contrast to those lacking easy atom movement characterized as 'inert'^{5,6}. Coordination complexes of vanadyl ion VO(II) are interesting as candidate chemotherapeutic agents⁷.

Vanadium is a ubiquitous trace element (cellular concentrations 10^{-8} M in mammals), which is able to influence signal transduction cascades with extraordinary sensitivity at several regulatory points⁸. The importance of vanadium complexes in the medicinal applications⁹ attracted attention in many applications such as material and organic syntheses¹⁰, therapeutic, medicinal immense¹¹ as anticancer^{12,13}, anti-diabetes¹⁴ effects on various enzymes

and speciation in human serum¹⁵. Vanadium complexes are high effective and selective catalysts for various homogeneous and heterogeneous oxidation processes of unsaturated hydrocarbons¹⁶.

Vanadium ions have numerous structural roles reflected by its structural and electronic analogy to phosphate^{17,18}. Vanadium has different coordination modes and high affinity for nitrogen, oxygen and sulfur donor atoms¹⁹. In this work, our aims are to prepare and characterize vanadyl VO(II) complexes with o-phenylenediamine (OPD) ligand and use the prepared complexes as a chemotherapeutic agent, catalysis and insulin mimic compound in future study. The structure of o-phenylenediamine (OPD) is depicted in fig.1.

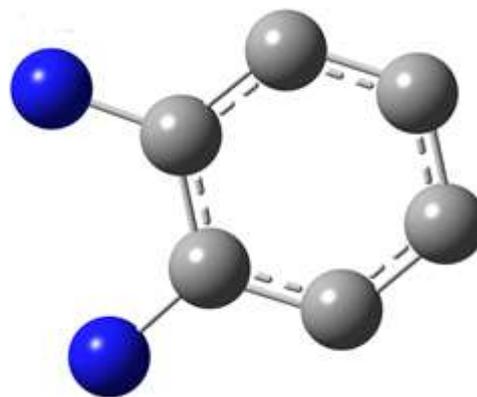


Fig. 1: Structure of the o-phenylenediamine ligand

Material and Methods

Materials: Chemicals used in this study were of the highest purity; o-phenylenediamine (OPD) (97%) was used without any purification and was purchased from Aldrich. Vanadyl VO(II) sulfate pentahydrate ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$) was purchased from Fluka. All solvents were of analytical grade.

Measurements: Infrared measurements of the complexes, as KBr pellets, were carried out using a Shimadzu (FT-IR)-8400S spectrophotometer in the range $400\text{--}4000\text{ cm}^{-1}$ in College of Sciences, University of Baghdad. Mass spectrometry measurements were carried out using GCMS-QP1000EX Shimadzu in Aksaray University scientific and technical research and application center. The magnetic susceptibility of the prepared complexes in the solid state was carried out using a Balance Magnetic Susceptibility Model (MSB-MKI) in College of Sciences, University of Baghdad. UV-Vis Spectra were recorded in a 1.0 cm path length quartz cell by using a UV-Vis spectrophotometer

type Shimadzu UV-1800 UV-Vis at 10^{-4} M contraction in DMSO in College of Sciences, University of Baghdad.

Conductivity measurements were carried out by Philips PW digital meters conductivity in DMSO at 10^{-3} M contraction in Department of Chemistry, College of Science for women, University of Baghdad. Melting point was determined by using (Stuart-melting point apparatus).

Preparation of the $[(VO(H_2O)_2(OPD))_2](SO_4)_2 \cdot 3H_2O$ complex (1) and $[(VO(OPD)_2)_2](SO_4)_2 \cdot 2H_2O$ complex (2).

0.108 g, 1.0 mmol and 0.216 g, 2.0 mmol of o-phenylenediamine (OPD) were dissolved separately in 10 mL of ethanol and slightly added to 0.253 g, 1.0 mmol of $VOSO_4 \cdot 5H_2O$ dissolved in 10 mL of distilling water in 1:1 and 1:2 M: L mole ratio. The mixtures of complexes have been adjusted to pH 8 by use of sodium acetate (0.136 g, 1.0 mmol) and (0.272 g, 2.0 mmol). The complexes were refluxed for 4 hours under constant stirring. The obtained solid complexes were filtered off, washed with warm water, ethanol, diethylether and dried in vacuum dissector for 24 hours. Complex (1) was deep red (yield: 67%), m.p >300 C° and complex (2) was deep red (yield: 90%), m.p >300 C°.

Results and Discussion

The analytical spectroscopic data of the vanadyl VO(II) complexes are given in table 1. The complexes were air stable and exhibited very good solubility in 1,4-dioxane, acetone. The molar conductance measurements were found to be 76.71 and 82.07 $Ohm^{-1}cm^2 \cdot mol^{-1}$ for complexes (1) and (2) respectively indicating that the complexes were electrolyte. This is in accordance with the fact that conductivity values for an electrolyte are 70-80 $ohm^{-1}cm^2 \cdot mol^{-1}$ in DMSO solution ²⁰.

FT-IR spectra: The FT-IR peaks of the complexes are given in table 2. The peaks of complexes are compared with that of free ligands in order to monitor the changes in the vibration frequency of the coordination sites. The spectra of the o-phenylenediamine (OPD) show bands at 3383-3364 cm^{-1} assigned to the stretching vibrations of the NH_2 groups. In the spectra of the vanadyl VO(II) complexes, the above-mentioned bands are shifted to lower frequencies at 3379-3210 cm^{-1} . This indicates the involvement of the NH_2 groups in the coordination of complexes. Coordination of the NH_2 groups is also confirmed from the shifts of their deformation vibrations found at 1150-1134 cm^{-1} for (ρtNH_2), 1115-1072 cm^{-1} for (ρwNH_2) and 826-822 cm^{-1} for (ρrNH_2) to lower frequencies ²¹.

Table 1
The analytical properties of the VO(II) complexes

Complex	Molar mass	Mass Spec. m/z (P ⁺)	Λ_m $Ohm^{-1}cm^2 mol^{-1}$	μ -effect B.M	UV-Vis. absorption peaks (nm)
$[(VO(H_2O)_2(OPD))_2](SO_4)_2 \cdot 3H_2O$ (1)	668.36	66.37	76.71	3.20	290 319 399-440 531-585 Intra ligand ($\pi \rightarrow \pi^*$) Intra ligand ($n \rightarrow \pi^*$) LMCT d-d electronic transition ${}^2B_2 \rightarrow {}^2A_1$, ${}^2B_2 \rightarrow {}^2B_1$ ${}^2B_2 \rightarrow {}^2E$,
$[(VO(OPD)_2)_2](SO_4)_2 \cdot 2H_2O$ (2)	794.58	793.39	82.07	3.54	281 300 402-450 500-590 Intra ligand ($\pi \rightarrow \pi^*$) Intra ligand ($n \rightarrow \pi^*$) LMCT d-d electronic transition ${}^2B_2 \rightarrow {}^2A_1$, ${}^2B_2 \rightarrow {}^2B_1$ ${}^2B_2 \rightarrow {}^2E$

Table 2
FT-IR data (wave-number) cm^{-1} of ligand and its metal complexes

Compound	$\nu(O-H)$ hydrated	$\nu(NH_2)$	ρtNH_2	ρwNH_2	ρrNH_2	$\nu(V=O)$	$\nu(M-N)$
o-phenylenediamine (OPD)	---	3383 3364	1153	1057	925	---	---
$[(VO(H_2O)_2(OPD))_2](SO_4)_2 \cdot 3H_2O$ (1)	3414	3233 3217	1150	1072	826	972	501
$[(VO(OPD)_2)_2](SO_4)_2 \cdot 2H_2O$ (2)	3418	3379 3210	1134	1115	822	972	501

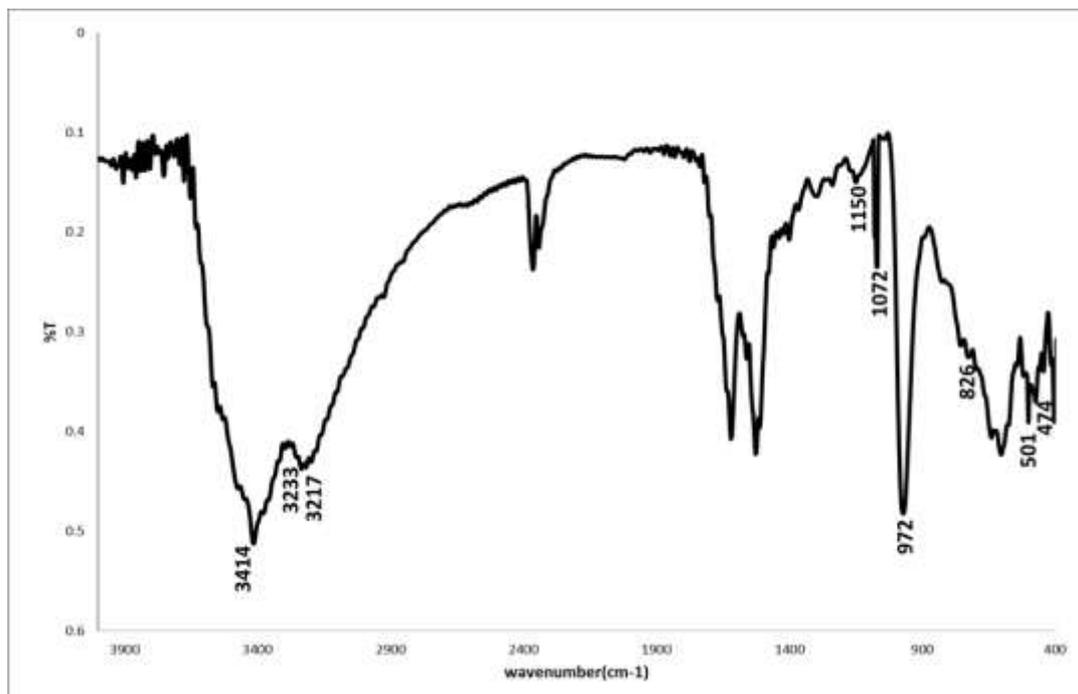


Fig. 2: IR spectrum of the $[(VO(H_2O)_2(OPD)_2)(SO_4)_2 \cdot 3H_2O]$ complex (1).

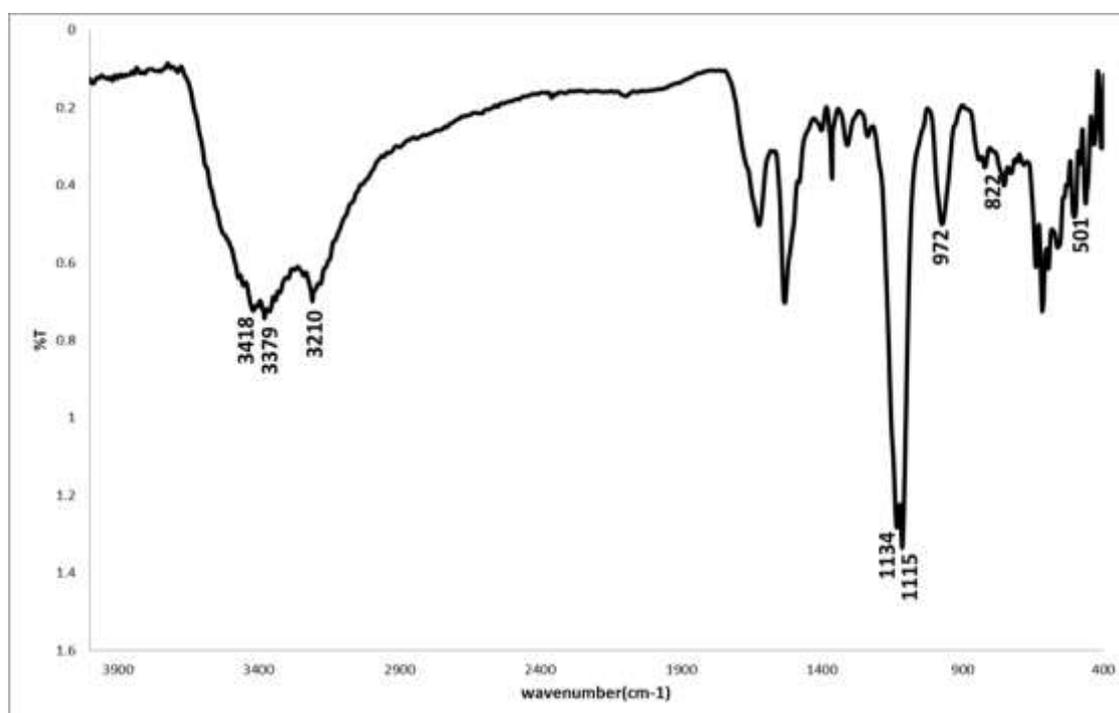


Fig. 3: IR spectrum of the $[(VO(OPD)_2)_2](SO_4)_2 \cdot 2H_2O]$ complex (2).

The spectra of complexes show new additional bands at 972 cm^{-1} assigned for the stretching of $\nu(V=O)^{22,23}$. The new band at 501 cm^{-1} may be assigned $M-N^{24}$. Finally, bands at 3414 and 3418 cm^{-1} are assigned to the hydrated water. The FT-IR spectra of the complexes (1) and (2) are presented in figs. 2 and 3.

Mass spectral analysis: The mass spectral data of the vanadyl VO(II) complexes show the major mass fragmentation peaks and are listed in table 3. Mass spectrum of the complex (1) (molecular weight 668.36) gave

molecular ion peaks [M] at $m/z = (666.37)$, a peak at $m/z = 422.90$ assigned for $(M-3H_2O, 2SO_4)$, a peak at $m/z = 366.08$ assigned for $(M-6H_2O, 2SO_4)$, a peak at $m/z = 352.08$ assigned for $(M-7H_2O, 2SO_4)$, a peak at 244.94 assigned for $(M-2H_2O, 2SO_4, OPD)$, a peak at 139.39 assigned for $(M-2H_2O, 2SO_4, 2OPD)$ and a peak at 73.06 assigned for (C_6H_4) . The spectrum of complex (2) (molecular weight 794.58) gave molecular ion peaks [M] at $m/z = (793.39)$, a peak at $m/z = 564.08$ assigned for $M-2H_2O, 2SO_4$, a peak at $m/z = 458.93$ assigned for $M-2H_2O, 2SO_4, OPD$, a peak at $m/z = 242.92$ assigned for $M-2H_2O, 2SO_4, 3OPD$, a peak at $m/z =$

132.92 assigned for M-2H₂O, 2SO₄, 4OPD and a peak at 73.03 assigned for C₆H₄²⁵. The mass spectra indicated that all the vanadyl VO(II) complexes are separated as dinuclear

associated with hydrated water. Mass spectra of the complex (1) and (2) are presented in figs. 4 and 5.

Table 3
Mass fragments data of vanadyl VO(II) complexes

Complex	Molar mass	Important mass fragmentations (m/z) values
[(VO(H ₂ O) ₂ (OPD)) ₂](SO ₄) ₂ .3H ₂ O (1)	668.36	666.37 (M), 422.90 (M-3H ₂ O, 2SO ₄), 366.08 (M-6H ₂ O, 2SO ₄), 352.08 (M-7H ₂ O, 2SO ₄), 244.94 (M-2H ₂ O, 2SO ₄ , OPD), 139.39 (M-2H ₂ O, 2SO ₄ , 2OPD) 73.06 (C ₆ H ₄).
[(VO(OPD) ₂) ₂](SO ₄) ₂ .2H ₂ O (2)	794.58	793.39 (M), 564.08 (M-2H ₂ O, 2SO ₄), 458.93(M-2H ₂ O, 2SO ₄ , OPD), 242.92 (M-2H ₂ O, 2SO ₄ , 3OPD), 132.92 (M-2H ₂ O, 2SO ₄ , 4OPD), 73.06 (C ₆ H ₄).

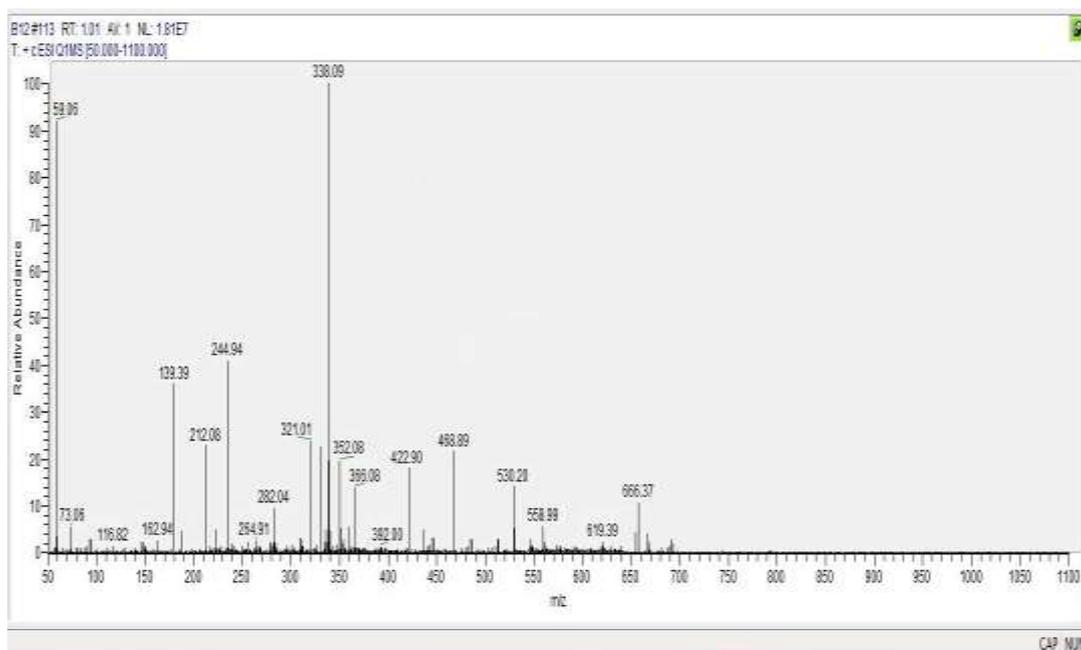


Fig. 4: Mass spectrum of the [(VO(H₂O)₂(OPD))₂](SO₄)₂.3H₂O complex (1).

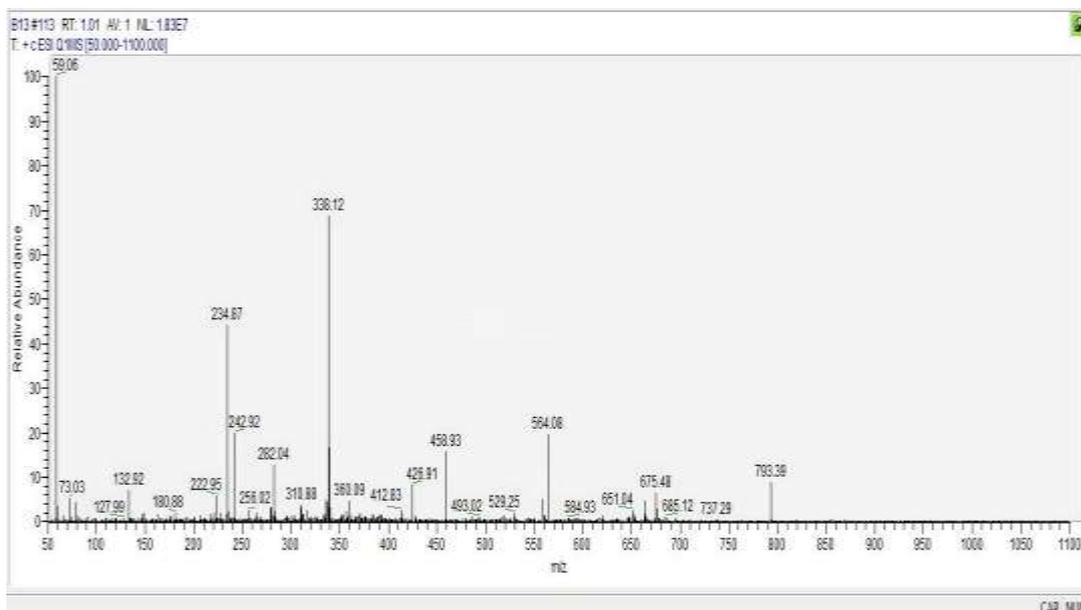


Fig. 5: Mass spectrum of the [(VO(H₂O)₂(OPD))₂](SO₄)₂.2H₂O complex (2).

Electronic spectra: The electronic spectral data of the VO(II) complexes in DMSO as solvent were recorded in the range 200–1100 nm and are given in table 1. The vanadyl VO(II) complexes exhibited absorption bands in the range (281-290) and (300-319) nm assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively in the benzene ring and diamine groups in the o-phenylenediamine ligand²⁶. The spectra show shoulders at (399–445) nm which are assigned to LMCT (ligand-to-metal charge transfer) within square pyramidal moieties¹⁹. The peaks in the visible region at (500–590) nm, are assigned to the d-d electronic transition type ${}^2B_2 \rightarrow {}^2A_1$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ of the vanadyl VO(II)

complexes²⁷. The UV–Vis spectra of the complexes are presented in figs. 6 and 7.

Magnetic susceptibility measurements: Measurements of the magnetic susceptibility of the vanadyl VO(II) complexes are tabulated in table 1. The effective magnetic moments of the vanadium (IV) complexes are 3.20 and 3.54 B.M for (1) complex and (2) complex respectively. These values are expected for VO(II) paramagnetic complexes with d^1 configuration²⁸. The proposed structures of prepared complexes are given in fig. 8.

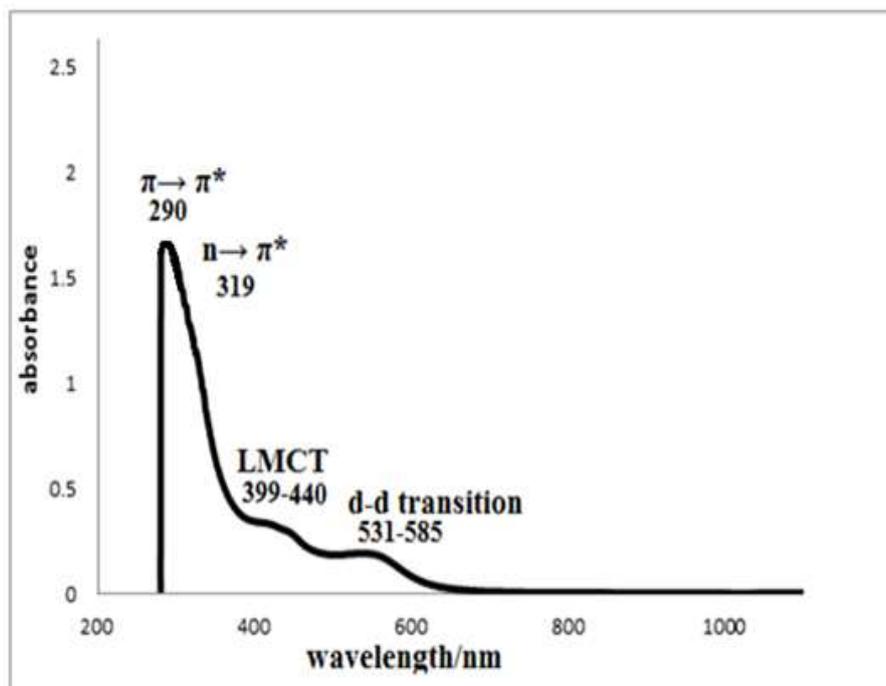


Fig. 6: UV-Vis. spectrum of the [(VO(H₂O)₂(OPD)₂](SO₄)₂·3H₂O complex (1).

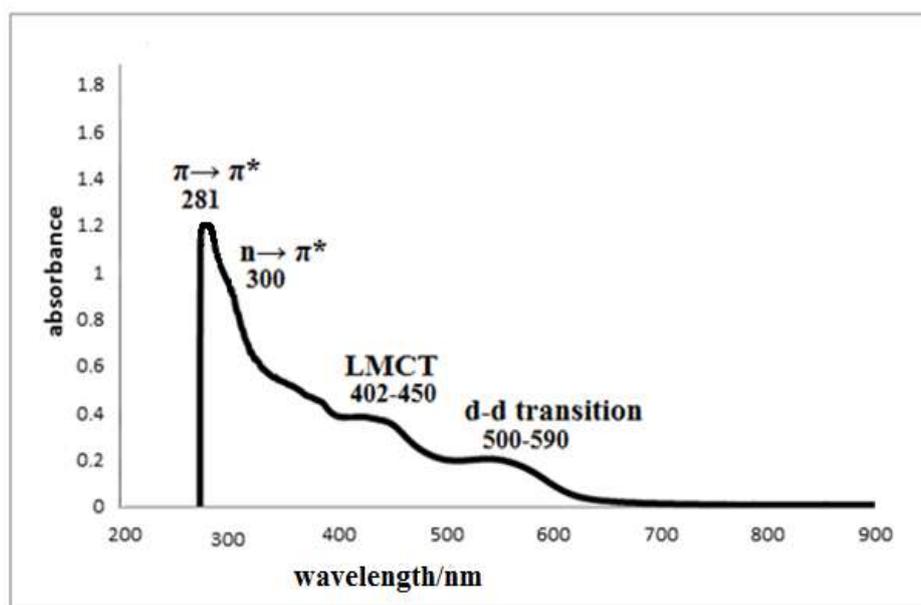


Fig. 7: UV-Vis. spectrum of the [(VO(H₂O)₂(OPD)₂](SO₄)₂·2H₂O complex (2).

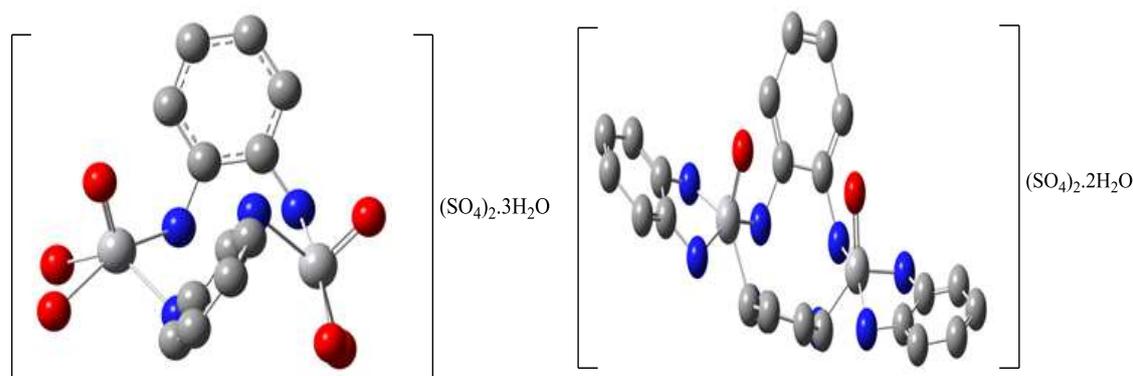


Fig. 8: The proposed structures of the vanadyl complexes (1-2). For simplicity hydrogen atoms have been omitted.

Conclusion

The vanadyl VO(II) complexes have square pyramidal geometry in which the o-phenylenediamine (OPD) acts as N₂ donor ligand and bond between two vanadium atoms as a bridge ligand. The spectroscopic data show that the o-phenylenediamine (OPD) coordinates through the nitrogen atoms and binds to vanadium atoms as bridge ligand. The magnetic susceptibility shows that the complexes are paramagnetic.

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